Office of Vehicle Technologies

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Overview and Progress of the Batteries for Advanced Transportation Technologies (BATT) Activity

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Project ID: ES 108

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Perform cutting-edge research on new materials and address fundamental chemical and mechanical instability issues.

Challenges

- Conduct research and development on the next-generation of battery anodes, cathodes, and electrolytes.
- Understand failure mechanisms to enable higher energy, longer lasting, and less expensive batteries.
- Conduct comprehensive modeling of cell and material behavior.

Participants

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BATT Structure

Current program consists of six tasks and two focus groups.

TASKS

- Electrode Architecture
- Anodes
- Cathodes
- Electrolytes
- Modeling
- Diagnostics

FOCUS Groups

- Silicon Anode Working Group
- High Voltage Working Group

Electrode Architecture (1)

The main goals of this task are:

- to benchmark state of the art materials: silicon anodes and high-voltage cathodes
- to provide high-quality electrodes to the BATT Program community
- to develop highly controlled electrode architectures to enable:
  - very high energy density electrodes using very low tortuosity electrode design
  - silicon anodes with a high capacity and long life

Anodes (2)

- Goal: move beyond graphite to develop high-energy anodes
- Focus: silicon materials
- Various strategies investigated to mitigate mechanical degradation and surface instability during charge/discharge cycles:
  - depositing Si on copper porous current collector
  - hollow silicon nanotubes, hollow spheres, yolk-shell structures
  - use of metal/Si alloys
  - mesoporous Si-sponges
  - Si/SiO_x graphene micro- and nanocomposites
  - atomic layer deposition coatings to improve electrode cohesion
- Exploration of exfoliated MAX phases

Anodes - Status

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Current emphasis: Generation of high-capacity Si nanocomposites, focused at controlling volume expansion/contraction as well as lithium and solvent consumption due to continued SEI formation with cycling.

Challenges

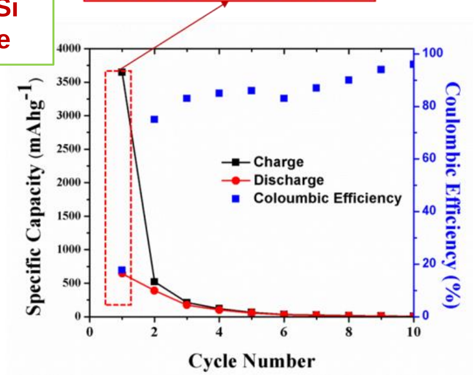
- **High 1st cycle irreversible loss**
  - Li loss with SEI formation
- **Low loading/areal capacity**
  - High reactivity of nano Si
- **High capacity fade**
  - Volume expansion/contraction
- **Low coulombic efficiency**
  - SEI formation
- **Poor rate capability**
  - Inadequate Li diffusion

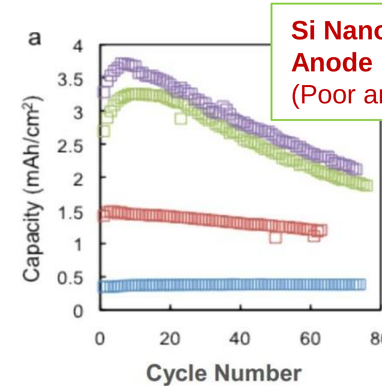
Approaches

- **Novel architectures:** Nanotubes, Nanowires, core-shell structures, composites
- **Functional coatings:** Metals, Li^+ and e- conducting ceramics, carbon based systems
- **Binders:** High strength and elastomeric polymers
- **Electrolyte additives:** VC, FEC

Bulk Si Anode

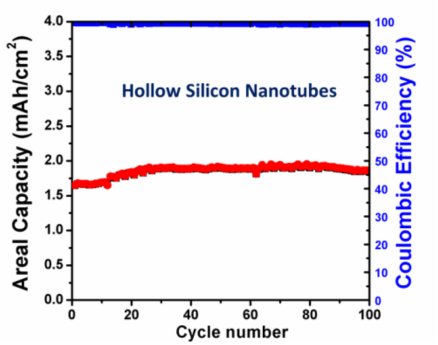
1st cycle irreversible loss

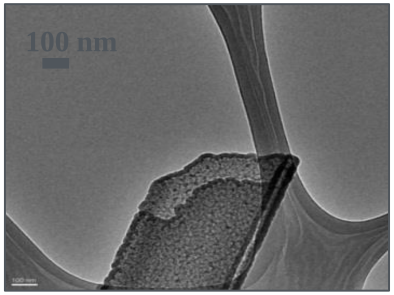




Si Nanoparticle Anode
(Poor areal capacity)

Novel architectures: Silicon Nanotubes





Si Nanotube: HRTEM

Si Nanotubes prepared by scalable approach show a high areal capacity (>1.5 mAh/cm^2) and good capacity retention

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Electrolytes (3)

- Electrolyte projects have a two-year duration
- Goals are to develop new electrolytes enabling new electrode materials generations:
  - high-voltage operations (4.6V)
  - compatible with silicon anodes

Cathodes (4)

- Critical need to develop high-energy cathode materials but no clear winner on the horizon
- Several approaches pursued:
  - Li_2MnO_3 stabilized composites
  - metal-doped NMC
  - polyanion materials having the capability to exchange more than one lithium ion
  - polyanion glassy materials
  - synthesis of metastable phases
  - aqueous catholytes (require conductive electrolyte separator)

Cathodes - Status

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Concentrated effort to search for high-capacity cathode materials – focused at solving voltage fade issue of Li-rich, “layered-layered” cathode material.

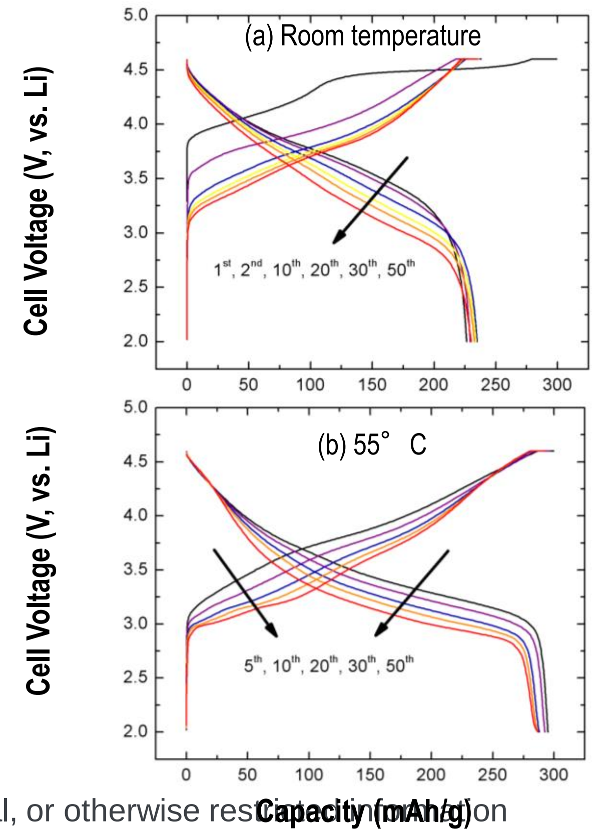
Challenges

- **Energy density of Li-ion cells**
  - Limited by the cathode performance – materials changed little over 20 years
- **Few alternative “next gen” cathodes**
  - Current cathodes are limited to 4.3V– electrolyte oxidation at high voltages
- **Excess Li material issues**
  - Exhibit promise, however face problems, including– voltage fade, high impedance, and low tap density

Approach

- **New Materials**: Understand reactivity at voltages above 4.3V and design new materials
  - Electrolytes to operate at high voltages
  - Additives to form artificial coatings on cathodes
  - Inorganic coatings to “protect” the cathode
- **Fundamental Knowledge**: Understand phase transformation in excess Li cathodes
  - Try to alleviate the voltage fade

Voltage profiles of Li/0.5Li_2MnO_3• 0.5$LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$ cells (cycled at C/15 rate)



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Diagnostics (5)

- The Diagnostics Task is essential to investigating performance-limiting and life-limiting processes in batteries
- Focus is to support effort on new electrode materials: silicon anodes and high-energy cathode materials
- One project on Li/S batteries: understanding the composition of polysulfide species generated during charge and discharge

Modeling (6)

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- Sophisticated mathematical modeling supports Tasks 1-5
- Brings physical understanding to complex interactions through development of comprehensive phenomenological models
- Current projects address:
  - atomistic degradation mechanisms for Li-excess materials
  - first principal calculations to understand capacity limitations
  - *ab initio* modeling of SEI formation and evolution on silicon anodes
  - calculation of stress/strain response of SEI and implications for mechanical degradation
  - measuring and predicting electronic and ionic conductivities of electrodes
  - mathematical modeling of Li/S batteries

Fluorinated Electrolyte for 5-V Li-Ion Chemistry

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PI/Co-PI: Z. Zhang (ANL) / K. Xu (US ARL) / X. Yang (BNL)

Technical Approach:

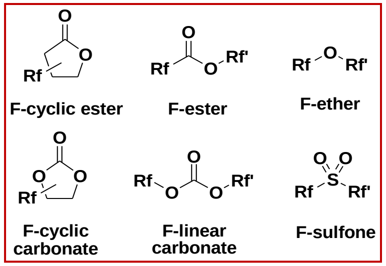
- Design and synthesize new electrolyte solvents with intrinsic oxidation stability and good ionic conductivity.
- Explore cathode passivation additives to further mitigate the surface reactivity on 5-V $LiNi_{0.5}Mn_{1.5}O_4$ spinel.
- Conduct *in situ* surface characterization (XAS, AFM, and XPS) to assist the rational design of electrolytes and additives.

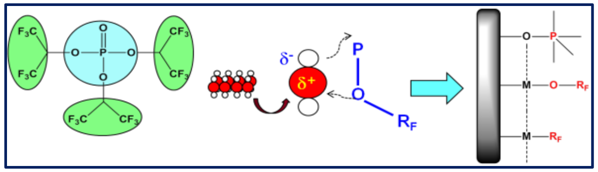
Status:

- Demonstrated the 1st generation fluorinated electrolyte with improved voltage stability.

Technology:

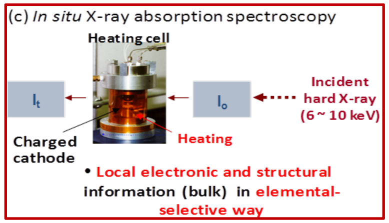
High voltage electrolytes based on fluorinated solvents and fluorinated additives for 5-V $LiNi_{0.5}Mn_{1.5}O_4$ and graphite cell. The intrinsic oxidation stability of the is offered by lowering the HOMO energy level with strong electron-withdrawing fluorine and fluorinated alkyl groups attached to the solvent structure.





Objectives:

- Develop a new electrolyte system with outstanding stability at high voltage and high T with improved safety characteristic.
  - Solvents with intrinsic stability (>5.0V vs Li+/Li)
  - Additives to compact & robust SEI
- Understand electrode/electrolyte interaction mechanism in:
  - LNMO/Graphite cell.
  - In situ XAS, AFM and XPS



Deliverables:

>95% capacity retention in 500 cycles for LNMO/graphite cells with improved safety characteristic; Fabricate twelve pouch cells (10mAh) with the optimal fluorinated electrolyte (solvents + additive) for DOE validation. (2 Years project, start: 10/1/13)

Funding: $1.0M (DOE)

Milestones:

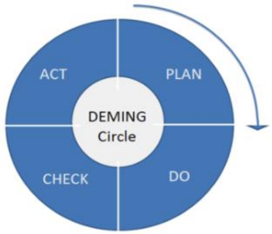
- **Q1:** Theoretical calculation of electrolyte solvents (fluorinated carbonate, fluorinated ether) and additives (fluorinated phosphate, fluorinated phosphazene); Validate electrochemical properties of available fluorinated solvents
- **Q2:** Synthesize/characterize Gen-1 electrolyte (3 linear/cylcic F-carbonate solvents + 1 additive) by NMR,FT-IR,GC-MS,DSC
- **Q3:** Evaluate LNMO/graphite cell performance of Gen-1 electrolyte [Solvent(s) + Additive(s)]
- **Q4:** Optimize Gen-1 high voltage F-electrolyte; Deliver 10 baseline pouch cells

Daikin America
High-Voltage Electrolyte

PI/Co-PI: Joe Sunstrom / Hitomi Miyawaki (Daikin)

Technical Approach:

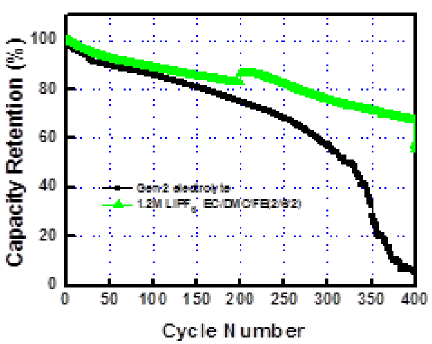
- Using a stable, established cell chemistry (4.6 V LMNO/graphite), we will conduct 4 PDCA cycles to develop a high-voltage electrolyte.
- 2 PDCA cycles to identify optimum base solvent and salt formulation utilizing basic property measurements
- 1 PDCA cycle to identify best available fluorinated anode/cathode additives which form stable SEI layers at high cell voltage
- 1 PDCA cycle to identify and optimize out gassing/acid scavenger additives
- Each PDCA cycle includes basic property measurements (conductivity, viscosity, electrochemical measurements and brief cycle testing in full cell test batteries



Status: First PDCA cycle underway

Technology:

Taking advantage of the inherent stability of fluorochemicals as compared to their hydrocarbon analogs, we are developing a n electrolyte with high voltage stability.



Cycle life performance at 55ºC for a LMNO/LTO cell containing conventional Generation 2 (black) and fluorinated FE (green) electrolyte.

Objectives:

Exploratory Development

- Identify promising electrolyte compositions for high-voltage (4.6 v) electrolytes via the initial experimental screening and testing of selected compositions

Advanced Development

- Detailed studies and testing of the selected high-voltage electrolyte formulations and the fabrication of final demonstration cells

Deliverables: Development of a stable (300 – 1000 cycles), high-voltage (at 4.6 volts), and safe (self-extinguishing) formulated electrolyte.

Funding:

- Duration: 2 yrs, Start: 10/1/13, Total: $1.29M, DOE: $912K Daikin America: $379K

Milestones (Due end of Budget Period 1: January 31, 2015)

- Complete high-voltage (4.6 V) electrolyte experimental design with consistent data sufficient to build models and identify promising electrolyte formulations
- Fabrication of 10 interim cells and delivery of cells to DOE
- Electrochemical and battery cycle tests are completed and results are obtained which demonstrate stable performance at 4.6 volts

Novel Non-Carbonate Based Electrolytes for Silicon Anodes

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PI: Dee Strand (Wildcat Discovery Technologies)

Technical Approach:

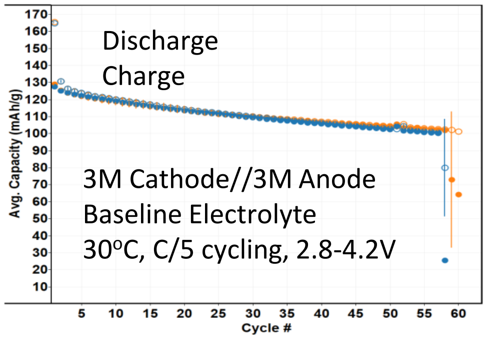
- Stage 1: Develop additive package to form stable SEI's on silicon anode
- Stage 2: Identify of non-carbonate solvents that are stable on additive-based SEI
- Stage 3: Optimize formulation to achieve voltage, conductivity targets

Status:

- Method validation complete to ensure 3M silicon anode results are replicated in Wildcat cells
- Mapping of additive performance on silicon vs. graphite in progress
- Solvent screening in progress to determine baseline solvent for additive testing

Technology:

Baseline data for 3M silicon alloy anode established for Wildcat cell architecture



Objectives:

- Development of non-carbonate electrolyte formulations that:
  - Form stable SEIs on 3M silicon alloy anode, enabling coulombic efficiency > 99.9% and cycle life > 500 cycles (80% capacity) with NMC cathodes
  - Have comparable ionic conductivity to carbonate formulations
  - Are oxidatively stable to 4.6V
  - Do not increase cell costs

Deliverables: Delivery of 10 interim and 10 improved 18650 cells and test protocols to specified DOE lab for testing

Funding:

- Duration: 2 yrs, Start: 10/1/13, Total: $1.25M, DOE: $999.8K, Industry: $249.9K

Milestones:

- Q1: Assemble materials, establish baseline performance with 3M materials.
- Q2: Develop initial additive package using non-SEI forming solvent.
- Q3: Screen initial solvents with initial additive package.
- Q4: Design/build interim cells for DOE.

FY 2014 BATT Funding Opportunity Announcement

- Solicit new proposals for beyond lithium ion technologies
- Primary Focus on:
  - Li metal protection
  - Solid electrolytes
  - Sulfur Cathode
  - Oxygen Cathode
  - Other non lithium chemistry

- Award selection will be announced in August